

# Visualization of heterogeneous oxygen storage in platinum-supported cerium-zirconium oxide three-way catalyst particles by hard X-ray spectro-ptychography

Heterogeneous solid catalysts are key materials in various chemical processes in modern industry, and the intrinsic nanoscale complexity of their heterogeneous structures has led to various discussions on their structure–activity relationships. The most typical form of solid catalysts is a powder, which is an assembly of nonuniform particles with different sizes, morphologies, atomic components, surface structures, and mesoscopic domains. The nanoscale complexity of their structural parameters is considered to be a reason for their unique catalytic performances.

Ce-based mixed oxides such as  $\text{CeZrO}_x$  are widely used as co-catalysts in three-way exhaust processes to expand the operation window. In particular,  $\text{Ce}_2\text{Zr}_2\text{O}_x$  ( $7 \leq x \leq 8$ ) solid-solution oxide with an ordered arrangement of Ce and Zr has been reported to exhibit excellent oxygen storage capacity (OSC) performance, where approximately 90% of the bulk Ce atoms are used in the redox process between  $\kappa$ -phase  $\text{Ce}_2\text{Zr}_2\text{O}_8$  and pyrochlore  $\text{Ce}_2\text{Zr}_2\text{O}_7$ . Their oxygen storage behavior inside the bulk of the solid solution is a key factor in its OSC.

X-ray imaging techniques, such as scanning X-ray microscopy using highly focused beams, are promising tools for imaging both structures and chemical states by combining them with the X-ray absorption fine structure (XAFS) method, i.e., using multiple energies around the absorption edge of a target element. The minimum probe size, which corresponds to the spatial resolution, in practical use is roughly 100 nm in the hard X-ray region, which is limited by the difficulty of

fabricating optical devices. X-ray ptychography can in principle overcome the limitations. In this approach, a sample is scanned across a coherent X-ray probe to collect the far-field coherent diffraction pattern at each beam position, and then images of both the sample and probe are reconstructed by iterative phase retrieval calculation [1]. X-ray ptychography using multiple energies including the absorption edge of a specific element, often referred to as X-ray spectro-ptychography (ptychographic XAFS), has been demonstrated in the soft X-ray region [2]. Extending this approach to the hard X-ray region enables us to visualize the chemical state inside micrometer-size bulk samples (Fig. 1). However, the absorption of incident X-rays is significantly small in the hard X-ray region, which makes it challenging to reach convergence in the conventional phase retrieval calculation. Recently, a phase retrieval algorithm using a constraint based on the Kramers–Kronig relation (KKR) has been proposed, and more quantitative images as well as X-ray absorption spectra have been experimentally obtained in the hard X-ray region [3]. In this study, we demonstrate the visualization of the Ce valence distribution of micrometer-size Pt-supported  $\text{Ce}_2\text{Zr}_2\text{O}_x$  (denoted as Pt/CZ- $x$ ,  $7 \leq x \leq 8$ ) particles with better than 50 nm resolution by ptychographic XAFS in the hard X-ray region [4].

The ptychographic XAFS measurements were performed using X-rays (5.717–5.817 keV, including the Ce  $L_3$  edge) at SPring-8 BL29XUL. 1 wt% Pt/CZ- $x$  particles (average CZ- $x$  particle size = 750 nm) were treated with  $\text{H}_2$  or  $\text{O}_2$  to prepare 1) Pt/ $\text{Ce}_2\text{Zr}_2\text{O}_7$

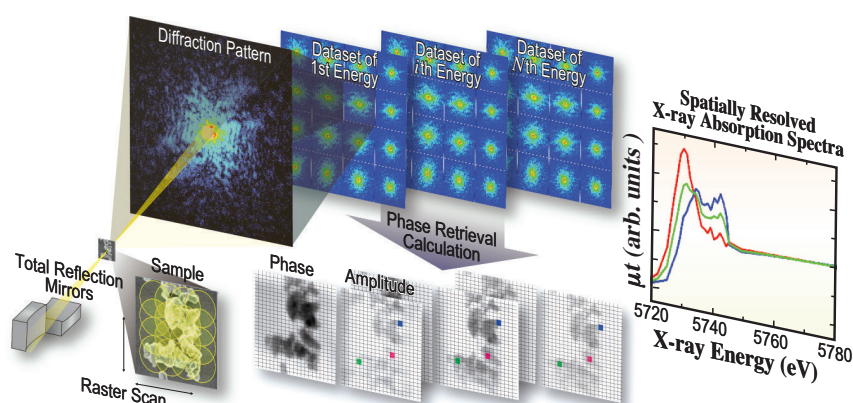


Fig. 1. Schematic of X-ray spectro-ptychography (ptychographic XAFS). A focused coherent X-ray beam is scanned across the specimen at multiple X-ray energies. Phase and amplitude images are reconstructed from diffraction patterns by phase retrieval calculation. By analyzing the energy dependence of the reconstructed images, spatially resolved X-ray absorption spectra are derived.

(denoted as Pt/CZ-7), fully reduced by  $H_2$  at 873 K; 2)  $Pt/Ce_2Zr_2O_8$  (denoted as Pt/CZ-8), fully oxidized by  $O_2$  at 773 K; and 3)  $Pt/Ce_2Zr_2O_{7.6}$  (denoted as Pt/CZ-7.6), prepared by the reaction of Pt/CZ-7 with  $O_2$  at 423 K. Incident X-rays were two-dimensionally focused to a 500 nm (full width at half maximum) spot size by a pair of Kirkpatrick–Baez mirrors, and then the samples were scanned in 9-by-9 positions with a step width of 400 nm. Multiple coherent diffraction patterns were collected using an in-vacuum pixel array detector with an exposure time of 4.0 s at each scan.

The amplitude and phase images were reconstructed using the ePIE algorithm with the KKR constraint [3]. Figures 2(a) and 2(b) show phase and amplitude images at 5.732 keV above the Ce  $L_3$  edge, respectively. On the basis of the phase retrieval transfer function, the full-period spatial resolution was estimated to be better than 50 nm at all X-ray energies. The shapes of the individual particles are in good agreement with the SEM and X-ray ptychography images. The Ce valence maps of each particle were then estimated by analysis of the ptychographic XAFS images. The XAFS spectra of Pt/CZ- $x$  ( $\mu t$ )<sub>CZ $x$</sub>  can be approximately expressed by a linear combination

of the normalized standard XAFS spectra of Pt/CZ-7 ( $\mu t$ )<sub>CZ7</sub> and Pt/CZ-8 ( $\mu t$ )<sub>CZ8</sub> as  $(\mu t)_{CZx} = a(\mu t)_{CZ7} + b(\mu t)_{CZ8}$ . The parameters  $a$  and  $b$  at each pixel were determined by a least-squares fit, and  $(3a + 4b)/(a + b)$  provides the Ce valence as presented in Fig. 2(c). While Pt/CZ-7 and Pt/CZ-8 particles were respectively almost fully reduced and oxidized as expected, partially oxidized Pt/CZ-7.6 particles exhibited a complicated valence distribution. The differences were thought to be caused by the inhomogeneous reactivity in the domain structures formed inside the particles.

In summary, we successfully reconstructed amplitude and phase images by ptychographic XAFS at 27 X-ray energies to obtain two-dimensional mappings of the Ce valence of Pt/CZ- $x$  particles with spatial resolution better than 50 nm. By coupling ptychographic XAFS with computed tomography measurement, three-dimensional structural and chemical nanoimaging is possible, which will elucidate the unrevealed intrinsic heterogeneous reaction behaviors of the material. We believe that the present approach will be a more promising and powerful tool in future synchrotron facilities, where a high coherent flux will be obtained.

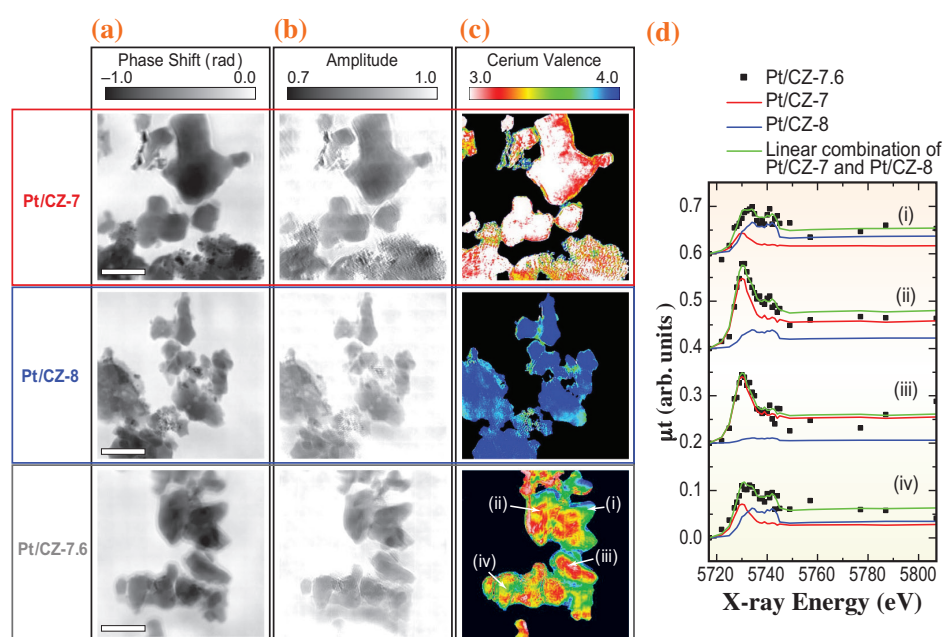


Fig. 2. (a, b) Phase and amplitude images at 5.732 keV. (c) Ce valence images. The pixel resolution is 13 nm and the scale bars represent 1  $\mu m$ . (d) One-pixel XANES spectra of Pt/CZ-7.6 at positions (i)–(iv) in (c). Red, blue, and green lines represent the fitted spectra of Pt/CZ-7 and Pt/CZ-8 and their linear combination, respectively.

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## References

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